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ARTICLE XVI.

Observations on Sulphurous Ether, and Sulphate of Etherine (the true Sulphurous Ether). By R. Hare, M. D., Professor of Chemistry in the University of Pennsylvania.

It is known that when two parts, by weight, of sulphuric acid are distilled with one of alcohol, a yellow sulphurous liquid is obtained. Berzelius alleges, that when this liquid is exposed in an exhausted receiver over sulphuric acid and hydrate of potash, an oleaginous liquid remains, which he designates as "*oil of wine containing sulphuric acid, or heavy oil of wine.*"

This oil is, by the same author, described as being heavier than water, as having a penetrating aromatic odour, and a cool pungent taste, resembling that of peppermint. It is, in fact, the liquid which Hennel first analysed as oil of wine, without, at the same time, mentioning the process by which it was procured. No doubt the difference between it and that procured by Boullay and Dumas, was, in some degree, the cause of the discordance between his observation and theirs. According to Hennel, the oil of wine consists of an atom of sulphuric acid, and an atom of hydrocarbon: $\ddot{S} + 4C + 4H$. By the last mentioned appellation, this skilful chemist designates a compound consisting of four atoms of carbon, and four of hydrogen.

Serullas represents the oil in question as consisting of two atoms of the acid, two of hydrocarbon or etherine, and one of water.

To the hydrocarbon of Hennel (4 C H), as the common base of all the ethers, excepting those lately alleged to have mytheline for a base; the name of etherine has been given; so that the heavy oil of wine may be called the sulphate of etherine: or, according to the formula of Serullas, $2\ddot{S}E+H$, it is a hydrous sulphate of etherine. It is, in fact, the only compound to which the name of sulphuric ether can be applied with propriety. The yellow liquid out of which it is procured, as above stated, may be designated as the ethereal sulphurous sulphate of etherine.

Another oil, lighter than water, resulting from the distillation of the ethereal sulphurous sulphate of etherine, from hydrate of lime, or from potash, is described by Berzelius as oil of wine exempt from sulphuric acid. Of this the odour is represented as disagreeable; and, though nothing is said of its taste, it is to be presumed that it differs from the heavy oil of wine in this respect, as well as in its odour and specific gravity.

Thènard alleges, that when the heavy oil of wine is heated with water for some time, a liquid swims on the water, which, if refrigerated by ice, will, within twenty-four hours, deposit crystals. The mother liquid he calls light oil of wine, while to the crystals he gives the name of concrete oil of wine. Hennel mentions his having obtained a similar product by the reaction of oil of wine with water, or an aqueous solution of potash; and treats the crystalline matter as the base of the heavy oil of wine, deprived of its acid; or, in other words, as his "hydrocarbon;" or, as above mentioned, etherine.

Considering how much has been written on this topic, I am surprised that I have met with no statements respecting the reaction of ammonia with the above mentioned ethereal sulphurous sulphate of etherine.

Since the year 1818, I have been accustomed to saturate the acid in that liquid by ammonia. The residue, being rendered very fragrant, and entirely freed from its sulphurous odour, by admixture with about twenty-four parts of alcohol, was found to constitute an anodyne, possessing eminently all the efficacy of that so long distinguished by the name of Hoffman. When the residue, remaining after satu-

ration with ammonia, was distilled in a water bath, ether came over, and left an oil which I was accustomed to consider as the oil of wine.

I had observed that, in the process above mentioned, there was a striking evolution of vapour, which seemed irreconcilable with the received opinion of the re-agents employed. Since the affinity between the ammonia and sulphurous acid is energetic, it did not appear to be reasonable that a copious escape of the one should be caused by its admixture with the other; and it was no less improbable that the vaporization of hydric ether, in its natural state, could take place at temperatures so much below its boiling point as those at which this phenomenon was noticed. In order to ascertain the truth, I luted a funnel, furnished with a glass cock and an air tight stopple, into the tubulure of a retort, of which the beak was so recurved downwards as to enter and be luted into the tubulure of another retort. The beak of the latter passed under a bell over water.

Both retorts were about half full of liquid ammonia, and surrounded with ice. The apparatus being thus arranged, about a thousand grains of the ethereal sulphurous sulphate of etherine were poured into the funnel, and thence gradually allowed to descend into the ammonia in the first retort. Notwithstanding the refrigeration, much heat was perceptible, and a copious evolution of vapour, which, passing into the second retort, was there absorbed or condensed, none being observed to reach the bell glass. At the close of the operation, hydric ether, holding oil of wine in solution, floated upon the ammonia in the first retort, and pure ether, of the same kind, floated on the ammonia in the second.

The ammonia in both retorts gave indications of the presence of sulphurous acid, on the addition of sulphuric acid. From these results, I inferred that a chemical compound of sulphurous acid and hydric ether formed the principal portion of the yellow liquid, and might be separated by distillation. Accordingly, by means of retorts arranged and refrigerated as above described, I procured a portion of sulphurous ether, which boiled at 44°, and which, when agitated with ammonia in a bottle, produced so much heat and consequent vapour, as to expel the whole contents in opposition to the pressure of my thumb. By employing the same distillatory apparatus, I subjected 2150 grains

of the ethereal sulphurous sulphate of etherine to distillation, and obtained 726 grains of sulphurous ether, which boiled as soon as the frigorific mixture was removed from the containing retort. This being redistilled, as in a former experiment, so as to receive the product in ammonia, left in the retort five grains of oil of wine. The resulting ammoniacal liquid, saturated with chloride of barium in solution, gave a precipitate which, agreeably to the table of equivalents, contained 356 grains of sulphurous acid.

The residue of the 2150 grains of ethereal sulphate being subjected to distillation, raising the temperature from 95°, the point at which it had been before discontinued, to 140°, the product obtained by means of a refrigerated receiver weighed 602 grains. This was, of course, inferior in volatility to the first portion distilled; and, when redistilled, it was found to contain a small quantity of oil of wine. In fact, it appears, the boiling point of the ethereal sulphurous sulphate rises, not only as the ratio of the sulphurous acid lessens, but also as the proportion of oil of wine augments.

The residual liquid being exposed to the heat of a water bath at 212°; a very fragrant, and well flavoured oil of wine was evolved, and floated upon a quantity of water acidulated by sulphuric or sulphovinic acid.

Agreeably to another experiment, 1750 grains by weight, of the ethereal sulphurous sulphate of etherine, after washing with ammonia, gave 869 grains of an ethereal solution of oil of wine. This being subjected to distillation by a water bath raised gradually to 190°, there remained in the retort 148 grains of oil, beneath which there were a few drops of acidulated water. Agreeably to the result of several experiments, the ethereal sulphurous sulphate of etherine yields about half its weight of the ethereal solution of oil of wine. The quantity is always somewhat less than half when weighed; but the deviation is not greater than might be expected to result from the loss by evaporation, and the diversity of refrigeration employed in the condensation of the ethereal sulphurous sulphate, during the process by which it is evolved.

Under the expectation of procuring a sulphurous ether of a still higher degree of volatility, I associated with the apparatus usually

employed in the process for generating hydric ether, a series of tubulated retorts, of which the beaks were recurved downwards in such a manner that the beak of the first communicated with a perpendicular tube, passing through an open-necked cylindrical receiver, so as to enter the tubulure of the second retort, of which the beak was in like manner inserted into a tube passing through a receiver in a third retort, and this communicated in like manner with a fourth retort. The second, third and fourth retorts, and the tubes entering them, were all refrigerated, the first with ice, the second with ice and salt, and the third with ice and chloride of calcium.

By these means, on subjecting to distillation in the first retort 48 ounces of alcohol of 830, and a like weight of sulphuric acid, besides the ethereal sulphurous sulphate of etherine usually resulting from the process, and condensing in the first receiver, it was found that in the other retorts severally, there were liquids of various degrees of volatility. That in the last boiled at 28°, but the boiling points rose gradually as the quantity of the residual liquid diminished.

In order to ascertain the nature of the sulph-acids abstracted from the ethereal sulphurous sulphate of etherine by the ammonia employed, chloride of barium was added in excess to the resulting ammoniacal solution, until no further precipitate would ensue. The liquid having been rendered quite clear by filtration, soon became milky. By evaporation to dryness, and exposure to a red heat, a residuum was obtained which proved partially insoluble in chlorohydric acid, and by ignition with charcoal, yielded sulphide of barium. It appears, therefore, that a hyposulphate of barytes existed in the liquid after it was filtered; as I believe that the hyposulphuric acid is the only oxacid of sulphur which is capable of forming with barytes a *soluble* compound, susceptible, by access of oxygen, of being converted into an insoluble sulphate, and precipitating in consequence.

It must be evident from the facts which I have narrated, that the yellow liquid obtained by distilling equal measures of sulphuric acid and alcohol, consists of oil of wine held in solution by sulphurous ether, composed of nearly equal volumes or weights of its ingredients; also, that the affinity between the *ether* and the acid is analogous to that which exists between alcohol and water. The apparent detection

of sulphuric acid in the ammonia, justifies a surmise, that the etherine distils in the state of a hyposulphate, which subsequently undergoes a decomposition into sulphurous acid and sulphate of etherine.

The liquid above alluded to, as resulting from the saturation of the ethereal sulphurous sulphate of etherine by ammonia, and distillation by means of a water bath gradually raised to a boiling heat, is a very fragrant variety of oil of wine. It differs from that described by Berzelius as the heavy oil of wine of Hennel and Serullas, in being lighter and containing less sulphuric acid. I have a specimen exactly of the specific gravity of water, and have had one so light as to float on that liquid. The oil of wine obtained by ammonia approximates, in its qualities, to the variety which Thènard describes as light oil of wine. The presence of sulphuric acid in a definite or invariable ratio does not appear requisite to the distinctive flavour or odour of oil of wine.

The heavy oil of wine treated by Hennel as sulphate of hydrocarbon, $2\ddot{S} + 4CH$; and by Serullas as a hydrous sulphate of etherine, $4CH + 2\ddot{S} + \dot{H}$; I have obtained, as above mentioned, by exposing the ethereal sulphurous sulphate of etherine, in vacuo, over the hydrate of lime, or potash, and sulphuric acid. This variety sinks in water, being of the specific gravity of 1.09 nearly; is of a deeper hue than the other, and of a smell less active, with a taste somewhat more rank. A specimen of oil thus obtained being subjected to the distillatory process, a portion came over undecomposed, leaving in the retort a carbonaceous mass. 14 grains of the oil which had not undergone distillation, and a like portion of the distilled oil, were severally boiled in glass tubes with nitric acid until red fumes ceased to appear; about 28 grains of pure nitre were added to each, some time before the boiling was discontinued. The resulting liquid was in each case poured into a platina dish, boiled dry, and afterwards deflagrated by a red heat. The residual mass being subjected to water, the resulting solution was filtered, an excess of nitric acid added, and then nitrate of barytes in excess.

The precipitate obtained from the distilled oil, weighed, when dry, only nine and five-eighths grains, while that procured from the oil which had not been distilled, amounted, under like circumstances, to fourteen and one-eighth grains. Ten grains of another portion, left for some

time over liquid ammonia, yielded only seven-eighths of a grain of sulphate.

About a drachm of Hennel's oil of wine was subjected to distillation with strong liquid ammonia; fourteen and a half grains came over, retaining the appropriate fragrance and flavour. This yielded, by the process above described, only two grains of sulphate of barytes. After all the water and ammonia had distilled, the receiver was changed, and fourteen grains of oil, devoid of the fragrance and flavour of the oil of wine, were obtained. This yielded one and one-eighth grains of sulphate. A carbonaceous mass, replete with sulphuric acid, remained in the retort.

Hennel states that when oil of wine was heated in a solution of potash, an oil was liberated which floated upon water, having but little fluidity when cold; and which, in some cases, partially crystallized. When gently heated, it became clear, and of an amber colour. The vapour had an agreeable, pungent, aromatic smell. This oil must have been pure etherine.

It is not improbable that this oil, which may be considered as devoid of sulphuric acid, is more or less liberated in evolving oil of wine, according to the nature of the process employed; and that the oil alluded to by Thènard, and those procured by me by simple distillation, ebullition, or distillation with ammonia or potassium, are mixtures of the etherine with its sulphate in various proportions. As it is well known that the odour of the essential oils is rendered more active by dilution, the livelier smell of the solutions may be consistent with a diminished proportion of the odoriferous matter.

Oil of wine cannot be distilled per se without partial decomposition, which does not take place below the temperature of 300. When subjected to the distillatory process, over potassium, at a certain temperature, a brisk reaction ensued, and the oil and metal agglutinated into a gelatinous mass. By raising the temperature the mass liquefied, and a colourless oil came over, which retained the odour of oil of wine. Meanwhile some of the potassium remained unchanged, and appeared within the liquid in the form of pure metallic globules. On pouring into the retort a portion of nitric acid in order to remove the caput mortuum, ignition took place from the presence of the potassium.